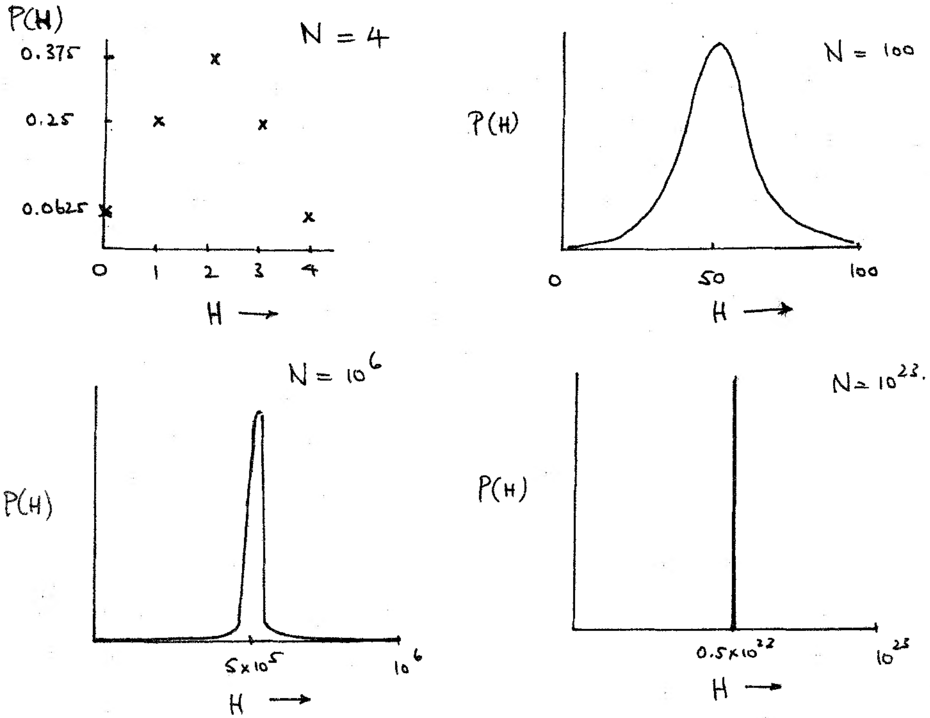
(21) Explanatory example.

Toss unbiased coin N times $P(H)$ = probability of H heads.



Taking across to distribution of particles problem.

Total number microstates Ω $\equiv$ area under curve.

Number of microstates in most probable distrib^n $t(N/2) \times 1$

See that for N very large $t(N/2) = \Omega$.

In terms of statistical mechanics.

Most probable distribution $\{n_j^*\}$

Number of microstates in this $t(\{n_j^*\}) \equiv t^*$

From above illustration $t^* = \Omega$. See problem sheet.

(2) Find most probable distribution $\{n_j^*\}$

Want maximum t (drop * now)

Work with $\ln t$ rather than t

(Allowable).

Recap. $$t = \frac{N!}{n_1!\, n_2! \, \dots \, n_j!}$$

Then

$$\ln t = \ln N! - \ln n_1! - \ln n_2! \dots \ln n_j!$$

$$= \ln N! - \sum_j \ln (n_j)!$$

For large N, n_j ...

can use Stirling's approx.

$$\ln N! = N \ln N - N$$

(See Guenault Appendix 2)

Then

$$\ln t = N \ln N - N - \sum_j (n_j \ln n_j - n_j)$$

Maximise $\ln t$

$$d(\ln t) = 0 = -\sum_j \left(\ln n_j + \frac{n_j}{n_j} - 1\right) dn_j$$

$$0 = -\sum_j \ln(n_j)\, dn_j$$

dn_j are changes in numbers of particles in states j — to get max $\ln t$.

But changing particles between states must obey

$$dN = 0 = \sum_j dn_j$$

$$dU = 0 = \sum_j \epsilon_j dn_j$$

To include these conditions – put into above equation multiplied by α, β respectively.

$$0 = -\sum_j \left(\ln(n_j) - \alpha - \beta\epsilon_j \right) dn_j$$

where α, β are factors to be determined.

dn_j now arbitrary

for above equation to be always true

$$\ln(n_j) - \alpha - \beta\epsilon_j = 0 \qquad \text{for each } j$$

Then $\quad \ln(n_j) = \alpha + \beta\epsilon_j$

$$n_j = \exp(\alpha + \beta\epsilon_j)$$

$$n_j = \exp\alpha \cdot \exp(\beta\epsilon_j)$$

This is most probable distrib^n

called Boltzmann distrib^n

Meaning of α.

Using $\quad n_j = \exp\alpha \, . \, \exp\beta\epsilon_j$

and $\quad \sum_j n_j = N$

Get $\quad N = \sum_j \exp\alpha \, . \, \exp\beta\epsilon_j$

$$N = \exp\alpha \sum_j \exp\beta\epsilon_j$$

$$N = A \sum_j \exp\beta\epsilon_j$$

$\exp\alpha = A$ normalises distrib[n] to N particles.

Thus $\quad n_j = A \exp\beta\epsilon_j$

$$n_j = \frac{N \exp\beta\epsilon_j}{\sum_j \exp\beta\epsilon_j}$$

(25) Meaning of β.

β must normalise distribution to total energy U.

Using

$$U = \sum_j n_j \epsilon_j = A \sum_j \epsilon_j \exp \beta\epsilon_j$$

get $$U = \frac{N \sum_j \epsilon_j \exp \beta\epsilon_j}{\sum_j \exp \beta\epsilon_j}$$

Form of β.

(i) Has units $(\text{energy})^{-1}$

(ii) For consistency with $S = k \ln \Omega$

need

$$\beta = -\frac{1}{kT}$$ (See Guenault p23)

where T defines temperature.

Recap.

Thermal equilibrium distribution is

Number of particles in state j $\left.\right\}$ $n_j = \dfrac{N \exp(-\epsilon_j/kT)}{\sum_j \exp(-\epsilon_j/kT)}$

Partition function Z.

Sum $\sum_j \exp(-\epsilon_j/kT)$ occurs often

Called $Z = \sum_j \exp(-\epsilon_j/kT)$

↓ partition f^n

or sum over states.

Bridge equations.

Equations linking macroscopic and microscopic descriptions

(1) $$S = k \ln \Omega$$

(2) For $U = \sum_j n_j \epsilon_j = \frac{N}{Z} \sum_j g_j \exp(\beta \epsilon_j)$

get $$U = \frac{N}{Z} \frac{dZ}{d\beta} = N \cdot \frac{d(\ln Z)}{d\beta}$$

(3) Using Helmholtz free energy F

$$F = U - TS$$

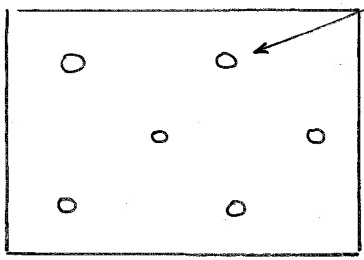
$$F = -NkT \ln Z$$ (See Guenault p 25)

Analyse particular systems.

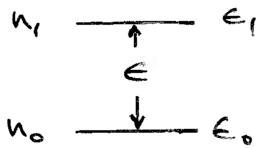
(i) Do analysis

(ii) Discuss comparison to real systems.

(i) Spin $1/2$ solid.



Contains some atoms that have 2 energy states



Ignore effect of rest of atoms.

Analysis.

Partition f^n $Z = \exp(-\epsilon_0/kT) + \exp(-\epsilon_1/kT)$

using $\epsilon_1 = \epsilon_0 + \epsilon$

get $$Z = \exp(-\epsilon_0/kT) + \exp(-\epsilon_0/kT)\exp(-\epsilon/kT)$$

$$= \exp(-\epsilon_0/kT)\left[1 + \exp(-\epsilon/kT)\right]$$

Level populations.

$$n_0 = \frac{N}{Z} \exp(-\epsilon_0/kT) = \frac{N \exp(-\epsilon_0/kT)}{\exp(-\epsilon_0/kT)\left[1 + \exp(-\epsilon/kT)\right]}$$

$$n_0 = \frac{N}{\left[1 + \exp(-\epsilon/kT)\right]}$$

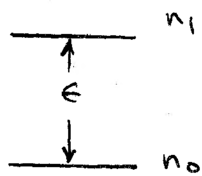
$$n_1 = \frac{N \exp(-\epsilon_1/kT)}{\exp(-\epsilon_0/kT)\left[1 + \exp(-\epsilon/kT)\right]}$$

$$= \frac{N \exp(-\epsilon/kT)}{\left[1 + \exp(-\epsilon/kT)\right]}$$

Graphs of n_0, n_1 versus temp T - see sheet.

Points

(i) For any 2 levels spaced by energy ϵ



$$n_1 = n_0 \exp(-\epsilon/kT)$$

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(ii) Extreme temp values of n_1, n_0

$T \rightarrow 0$ $\qquad \exp(-\epsilon/kT) \rightarrow \exp(-\infty) = 0$

$n_0 \rightarrow N$

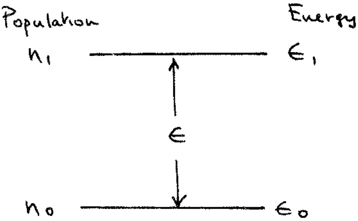
$n_1 \rightarrow 0$

$T \rightarrow \infty$ $\qquad \exp(-\epsilon/kT) \rightarrow 1$

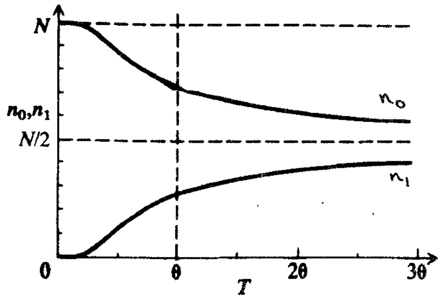
$n_1 = n_2 \rightarrow N/2$.

Analysis of 2 level system.

Variation with temp T



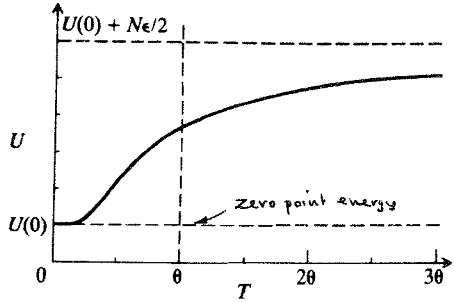
Level populations



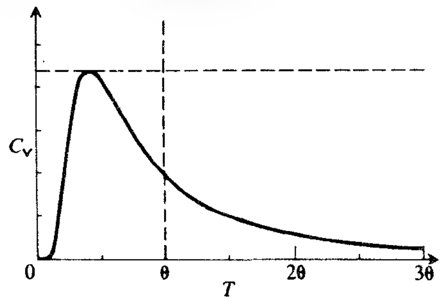
θ defined from

$$k\theta = \epsilon$$

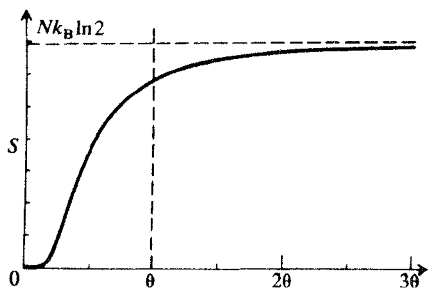
Energy.



Heat capacity



Entropy.



(31)

Energy U

$$U = n_0\epsilon_0 + n_1\epsilon_1 = n_0\epsilon_0 + n_1(\epsilon_0 + \epsilon)$$

$$= N\epsilon_0 + n_1\epsilon$$

$$U = N\epsilon_0 + \frac{N\epsilon \exp(-\epsilon/kT)}{[1 + \exp(-\epsilon/kT)]}$$

Defining temp θ by $k\theta = \epsilon$

Get $$U = N\epsilon_0 + \frac{N\epsilon \exp(-\theta/T)}{[1 + \exp(-\theta/T)]}$$

Graph of U versus temp T. – See sheet.

Points.

(i) Change in U at $T \sim \theta$

(ii) Temp extremes.

$T \to 0$ $\qquad U \to N\epsilon_0$

Called zero point energy

$T \to \infty$ $\qquad \exp(-\epsilon/kT) \to 1$

$U \to N\epsilon_0 + N\epsilon/2$

Heat Capacity C_V

Defined $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

Hence $C_V = \frac{\partial}{\partial T}\left\{ N\epsilon_0 + \frac{N\epsilon \exp(-\epsilon/kT)}{[1+\exp(-\epsilon/kT)]} \right\}$

Gives $C_V = N\epsilon \left\{ \frac{(\epsilon/kT^2)\exp(-\epsilon/kT)}{[1+\exp(-\epsilon/kT)]^2} \right\}$

Graph C_v versus T — see sheet.

Points

(i) Max at temp T where kT is same order as ϵ

(ii) Extreme temp limits

$T \to 0$ $\quad (\epsilon/kT^2)\exp(-\epsilon/kT) \to 0$

thus $C_V \to 0$

$T \to \infty$ $\quad \exp(-\epsilon/kT) \to 1 - \epsilon/kT$

$C_V \to N\epsilon^2/kT^2$

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Entropy S.

Since $F = U - TS$

$$dF = dU - TdS - SdT$$

$$dF = \underbrace{\cancel{TdS} - pdV}_{dU} - \cancel{TdS} - SdT$$

Thus $S = -\left(\frac{\partial F}{\partial T}\right)_V$

Bridge equation

$$F = -NkT \ln Z$$

$$= -NkT \ln\left\{ \exp(-\epsilon_0/kT)\left[1 + \exp(-\epsilon/kT)\right]\right\}$$

$$= -NkT \left\{\left(-\epsilon_0/kT\right) + \ln\left[1 + \exp(-\epsilon/kT)\right]\right\}$$

$$F = N\epsilon_0 - NkT \ln\left[1 + \exp(-\epsilon/kT)\right]$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = Nk \ln\left[1 + \exp(-\epsilon/kT)\right] + Nk\frac{(\epsilon/kT)\exp(-\epsilon/kT)}{\left[1 + \exp(-\epsilon/kT)\right]}$$

Graph of S vs T – see sheet.

Points.

Temp limits.

(i) $T \to 0$ $\quad \exp(-\epsilon/kT) \to 0$

$S \to 0$ $\quad$ all atoms in ground state

Number microstates $\Omega = 1$.

(ii) $T \to \infty$ $\quad \exp(-\epsilon/kT) \to 1$

$S \to Nk \ln 2$.

Connection with real systems.

Paramagnetic solid.

Identify chosen atoms as those with $S = 1/2$ and a magnetic moment. They are separated by many atoms with no moment.

Consider external field B applied

$S = \frac{1}{2}$ atoms have 2 possible alignments with B

Magnetic atoms have moment μ.

$B \uparrow \; \uparrow \mu$ or $B \uparrow \; \downarrow \mu$

energy $= -\mu B$ energy $= +\mu B$

energy difference $= \epsilon = 2\mu B$

Expressions for U, C_v, S apply with $2\mu B = \epsilon$

Further property – Magnetisation M.

M is magnetic moment induced by field B

N magnetic atoms.

Field B applied n_0 have $\mu \parallel B$

n_1 have μ opp to B.

Thus $M = n_0 \mu - n_1 \mu$

$$= \mu . \frac{N}{Z} \exp\left(\frac{\mu B}{kT}\right) - \mu \frac{N}{Z} \exp\left(-\mu B/kT\right)$$

$$M = N\mu \frac{\left[\exp\left(\mu B/kT\right) - \exp\left(-\mu B/kT\right)\right]}{\left[\exp\left(\mu B/kT\right) + \exp\left(-\mu B/kT\right)\right]}$$

(36)

Gives $M = N\mu \tanh(\mu B/kT)$

Graph M vs T — see sheet.

Points

(i) Limiting behaviour

For $\mu B \gg kT$ — large field, low temp.

$$\tanh(\mu B/kT) \rightarrow 1$$

$$M \rightarrow N\mu$$ — atoms fully aligned.

For $\mu B \ll kT$ — weak field, high temp

expand $\exp(\mu B/kT) = 1 + \frac{\mu B}{kT} + \cdots$

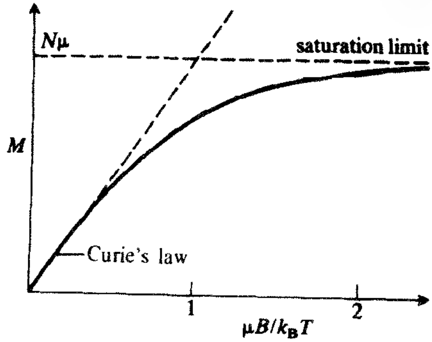
Get $$M = N\mu \frac{\left[1 + \frac{\mu B}{kT} + \cdots - \left(1 - \frac{\mu B}{kT} \cdots\right)\right]}{\left[1 + \mu B/kT + \cdots + 1 - \mu B/kT \cdots\right]}$$

$$M = N\mu . \frac{2\mu B}{2kT} = \frac{N\mu^2 B}{kT}$$

Curies Law for $S = 1/2$ paramagnet.

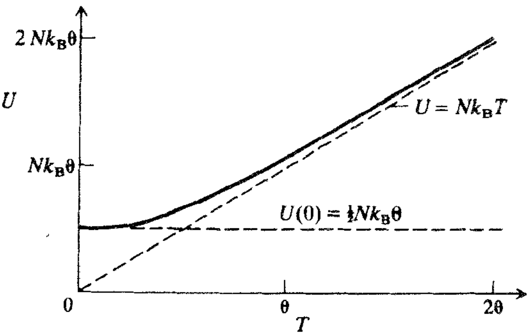
Paramagnetic solid

M versus $\left(\frac{\mu B}{kT}\right)$

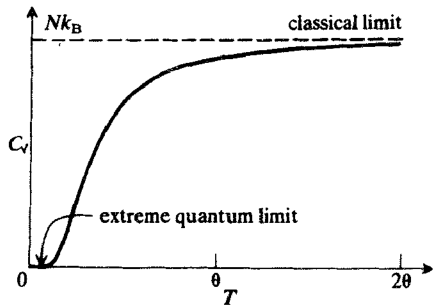


System of N one dimensional oscillators.

Energy.



Heat Capacity



(ii) For paramagnet with $S = 3/2, 5/2 \ldots$

Similar theory but more complicated.

General expression $M \rightarrow$ Brillouin f^n

Curie Law $M = N \dfrac{\mu^2 B}{3kT}$.

System 2. N localised 1D oscillators

Analysis

Quantum mechanical oscillator has energy states ϵ_j where

$$\epsilon_j = (j+\tfrac{1}{2})h\nu$$

h = Planck constant

ν = oscillator frequency

Thermal properties.

Partition f^n $$Z = \sum_j \exp\left(-\frac{(j+\frac{1}{2})h\nu}{kT}\right)$$

$$Z = \exp\left(-h\nu/2kT\right)\sum_j \exp\left(-j\frac{h\nu}{kT}\right)$$

$$Z = \exp\left(-\frac{h\nu}{2kT}\right)\left[1 + \exp(-h\nu/kT) + \ldots\ldots\ldots\right]$$

Geometrical Progression

Summed

$$Z = \exp\left(-\frac{h\nu}{2kT}\right) \cdot \frac{1}{\left[1 - \exp(-h\nu/kT)\right]}$$

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For U use bridge equation

$$U = N \frac{d(\ln Z)}{d\beta} \quad \text{where } \beta = -\frac{1}{kT}$$

In terms of β

$$Z = \exp\left(\frac{h\nu\beta}{2}\right) \cdot \frac{1}{[1 - \exp(+h\nu\beta)]}$$

$$\ln Z = \frac{h\nu\beta}{2} - \ln[1 - \exp(h\nu\beta)]$$

$$\frac{d(\ln Z)}{d\beta} = \frac{h\nu}{2} + \frac{h\nu \exp(h\nu\beta)}{[1 - \exp(h\nu\beta)]}$$

Thus $$U = \frac{Nh\nu}{2} + \frac{Nh\nu}{[\exp(h\nu/kT) - 1]}$$

Graph of U vs T – see sheet.

Limiting values

$T \to 0$ $\quad U \to \frac{Nh\nu}{2}$ (zero point energy)

$T \to \infty$ $\quad U \to NkT$ classical limit.

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Heat Capacity C_v.

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v$$

$$= \frac{\partial}{\partial T}\left\{ \frac{Nh\nu}{2} - \frac{Nh\nu}{\left[\exp(h\nu/kT) - 1\right]} \right\}$$

gives. $$C_V = \frac{Nk\left(h\nu/kT\right)^2 \exp\left(h\nu/kT\right)}{\left[\exp\left(h\nu/kT\right) - 1\right]^2}$$

Graph — see sheet.

Limiting values

$T \to 0 \qquad \exp\left(h\nu/kT\right) \to \infty \qquad C_V \to 0$

$T \to \infty \qquad \exp\left(h\nu/kT\right) \to 1 + h\nu/kT$

$$C_V \to Nk\left(h\nu/kT\right)^2 \cdot 1 \cdot \left(\frac{kT}{h\nu}\right)^2 \to Nk$$